ePProceedings Chemistry 4 (2019) 77-84

eISSN 2550-1453 http://eproceedings.chemistry.utm.my/

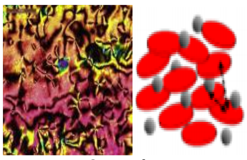
Effect of Silica on Director Alignment of 4-cyano-4'pentylbiphenyl Liquid Crystal

Rawaida Liyana Razalli[a], Che Rozid Mamat[a]*, Aishah Abdul Jalil[b], Siti Mariah Abd Wahab[b]

[a]*Department of Chemistry, Faculty of Science, Universiti Teknologi Malaysia, 81310 Johor Bahru, Malaysia*
[b]*School of Chemical and Energy Engineering, Faculty of Engineering, Universiti Teknologi Malaysia, 81310 UTM Johor Bahru, Malaysia*
**Corresponding Author: che@kimia.fs.utm.my*

Article history:
Received 20 June 2019
Accepted 18 July 2019

GRAPHICAL ABSTRACT



Nematic phase of 5CB at 25.0°C (left) and silica suspensions in 5CB host (right)

ABSTRACT

The application of liquid crystal can be look so advanced nowadays in the evolution of liquid crystal displays (LCDs).In this study, colloidal particles of silica, SiO2 were dispersed in the liquid crystal, 4-cyano-4‟-pentylbiphenyl (5CB) during isotropic phase. Various sets of SiO2 with different concentrations were prepared from 1 to 5 w/v%. The phase behaviour and morphologies of this silica colloidal liquid crystal were characterized by three different techniques, which are infrared spectroscopy (IR), polarized optical microscopy (POM) and electron spin resonance (ESR). The IR spectra revealed the presence of functional groups in the compounds indicating there are no chemical changes in which only physical interactions were involved when two different compounds were mixed together. The POM characterization was used to determine the presence of birefringence and the temperature of phase transition of liquid crystal and its hybrid system. The result showed the hybrid system exhibits nematic phase upon temperature at 25.0 °C. The ESR technique able to determine the director alignment of liquid crystal where it shows the director is affected by the silica concentration. The suspension of liquid crystal with low concentration of silica, 1 w/v% was found to align the director of liquid crystal in between of parallel and perpendicular to the magnetic field. By increasing the concentration of silica up to 5 w/v%, powder pattern was finally observed.

Keywords: Colloidal liquid crystal, 4-cyano-4'-pentylbiphenyl, birefringence, schlieren texture, powder pattern

1. INTRODUCTION

Liquid crystal is a matter which has properties of solid and liquid. It can flow like fluid and have arrangements of a lattice. In some substances, the tendency towards ordered arrangement is so high that on heating they pass through an intermediate state before forming clear liquid. This intermediate state is known as liquid crystal state. When temperature is applied, the liquid crystals are converted into isotropic liquid and become crystalline solid upon cooling. Therefore, liquid crystals have the characteristics of anisotropic properties and fluid that possess different properties. The rod-like shape of the structures itself as shown in Figure 1 could give strong interaction between them [1].

The researchers nowadays getting interested in the field of nanocomposites since they often expose unexpected properties of hybrid system. The problems found in liquid crystal display showing that the unclear motion image produced is not similar from the reality because of static or slower image occurred [2]. The display is affected by decreasing the contrast because the curve of voltage-brightness is not very sharp and the crosstalk of the 'sneak path' causing a ghosting effect [3]. The slower response time could also cause this effect to happen [4].

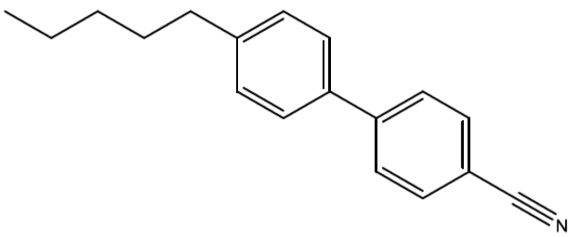


Figure 1. Chemical structure of liquid crystal, 4-cyano-4‟-pentyl-biphenyl (5CB)

To improve these drawbacks, silica powder is chosen to be dispersed in liquid crystal host. The phases of this hybrid system exhibit different charge affinities with the existence of an electric double layer at any surface. When an electric field is applied, the same charge of all particles will migrate to the electrode with a velocity proportional to the applied field strength. Steric repulsion is obtained when the particle surface is covered with bulky molecules. These molecules caused the colloidal particles to repel one another in the system. Spherical particles actually cause the formation of topological defects and disruption of the nematic phase [5]. These systems could exhibit interesting ordering and phase behaviour compared to the pure nematic host. In this study, the spherical structure of silica is mixed with 4-cyano-4'-pentylbiphenyl (5CB) nematic liquid crystal by addition of different concentration, 1 to 5 w/v% silica suspension to Liquid crystal matrices. The director alignment which is crucial to electro-optical display properties is studied using the powerful Electron Spin Resonance (ESR) and the liquid phase behaviours is determined by Polarized Optical Microscope (POM).

2. EXPERIMENTAL

2.1. Sample preparation and physical mixing of liquid crystal hybrid system

Approximately 0.05 g of pure nematic 5CB, purchased from Sigma Aldrich Co. (USA) was placed in a sample tube and the liquid crystal was heated by using hot air gun until it turns to isotropic phase. Next, the silica suspension, SiO_2 was added to the isotropic phase of the liquid crystal and stirred until homogenized. The suspension was prepared with various concentrations of silica from 1 to 5 w/v%. The samples were ready for the FTIR, POM and ESR characterization.

2.2. ESR characterization technique

The spin probe technique is used in ESR characterization due to liquid crystal is diamagnetic in nature. The 2,2,6,6-trimethylpeperidine-1-oxyl (TEMPO) was chose as the spin probe. For sample preparation, an approximately (0.5 ml) of the spin probe was dissolved in dichloromethane and placed into a sample tube. The lower concentration of 10^{-4} M of spin probe was managed to reduce the disruption of the spin probe towards the mesophase and the analysis provide information of liquid crystal through the spin probe spectrum. The 5CB nematic liquid crystal was heated and stirred with a magnetic stirrer for 15 min using hot plate/stirrer until the nematic changes to isotropic. Then, a glass pipette was used to transfer the mixture into the sample tube (15 cm in height and 5mm in diameter of the tube) in which the probe had already been added to the sample tube. It was easier to transfer the colloidal nematic while it in the isotropic phase since it is less viscous than in the nematic phase, especially for high concentrations colloids in nematic liquid crystal. The oxygen removal procedure was performed for 30 min by degassing using freeze-pump-thaw technique. The sample tube was sealed and ready for ESR measurement. The sample's result for ESR spectra were compared with the ESR spectrum of the spin probe in pure 5CB to see the changes of the director orientation of the liquid crystal.

3. RESULTS AND DISCUSSION

3.1. Characterization of SiO_2/5CB using infrared spectroscopy

ATR-IR spectrophotometer was used in this study by Perkin Elmer as the samples were in liquid forms. The IR spectra of pure 5CB and the hybrid system of 1 to 5 w/v% SiO_2/5CB were shown in Figure 2. Both pure 5CB and the hybrid systems shows absorptions peaks at 2856.66 and 2955.79 cm^{-1} indicating (C-H) stretching of the CH_2 groups of alkyl fragments and the peak at 2225.84 cm^{-1} represents the stretching vibration of the (C≡N) of nitrile group. The absorption peaks at 1605.70 and 1493.38 cm^{-1} represent the vibrations of C=C bonds in the benzene ring of the 5CB. For hybrid sample of 1 to 5 w/v% of SiO_2/5CB, not so much difference was observed. The peaks for all samples were identified belong to the functional groups of 5CB and the functional groups of $Si0_2$ do not appear in the spectrum. Overall, this gave information that the mixtures of two different compounds were having physical interaction since there was no functional group of SiO_2 presence in the IR spectra. The self-assembly process of this silica colloidal liquid crystal proved that the compounds were still pure.

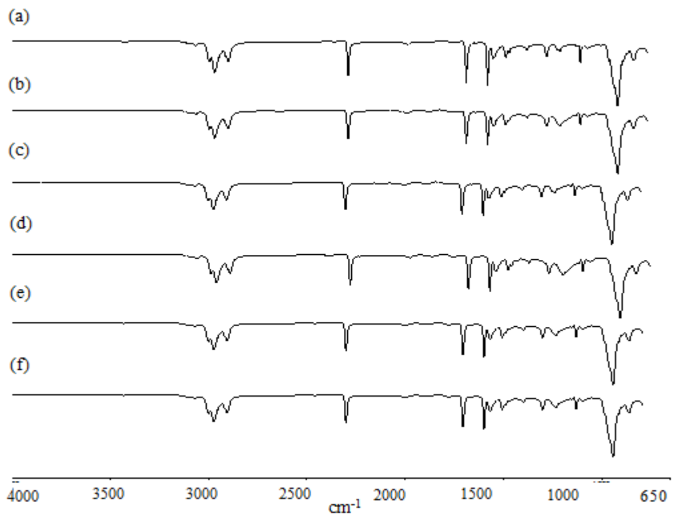


Figure 2. ATR-IR spectra IR spectra for (a) pure 5CB (b) 1 w/v% of SiO_2/5CB (c) 2 w/v% of SiO_2/5CB (d) 3 w/v% of SiO_2/5CB (e) 4 w/v% of SiO_2/5CB (f) 5 w/v% of SiO_2/5CB.

3.2. Characterization of SiO2/5CB using Polarized Optical Microscope (POM)

The observation of liquid crystal by a polarized optical microscope (POM) is necessary in order to reveal the mesophases display of the material. Birefringent samples especially the liquid crystals are most commonly studied using this technique. In each mesophase, the liquid crystals show specific pattern that is defined as “texture”. At 90 degree of the polarizer, the transmitted light from the sample can be blocked by it to the illumination. Heating stage is necessary to change the temperature of the samples at particular temperature range prior to this study. The images of pure 5CB and the hybrid system of 1 to 5 w/v% SiO_2/5CB were recorded at programmed temperature on heating and cooling process and shown in Figure 3.

The pure 5CB liquid crystals showed a nematic phase of liquid crystal at 25.0 °C. A schlieren texture of two and four brushes is observed as shown in Figure 3 (a) that assigned by certain strength, *s.* This gave information that most of the liquid crystal was aligned homeotropic (a spontaneous change in the preferred director orientation) to the glass substrates [6]. The dark line represents the liquid crystal molecules were aligned perpendicular to the glass surface or parallel to the polarizers [7]. Observation of a birefringent material between crossed polarizing filters reveals nematic patterns and color effects. The colors arise from interference between the ordinary ray and the extraordinary ray [8]. Further heating of the resulting sample induced a second transition from homeotropic to homogeneous alignment. Under POM, a uniform black indicated the complete destruction of light for isotropic phase as shown in Figure 3 (c). Thermal scenario of liquid crystal can be observed at temperature around 35.0 °C at which the phase transition occurred from nematic to isotropic phase as in Figure 3 (b). The birefringence of the newly formed region decreased with further increase of the temperature and nematic phase will start to form an isotropic. While, during cooling process, coloured bubbles appear due to the birefringence which is uniaxial. The material was considered as nematic once the bubbles can be seen. An example is shown in Figure 3 (d). The color changes of the materials due to light changes which had been polarized by the first filter of the microscope. The material shows colored display due to interference phenomena.

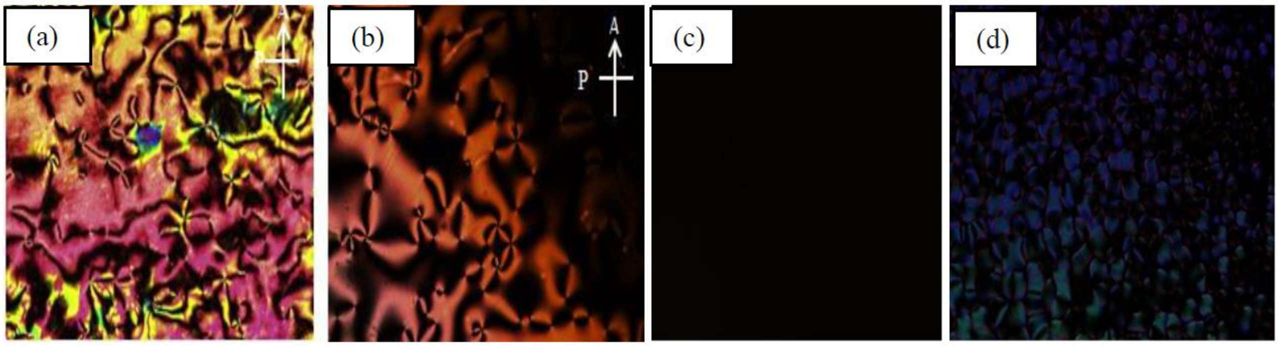


Figure 3. Images under POM of pure 5CB liquid crystal at various temperatures: (a) texture of nematic phase at 25.0 °C (b) nematic-isotropic phase transition at 35.0 °C (c) dark region of isotropic state during (heating) (d) isotropic-nematic phase at 35.0 °C (cooling). White arrows indicate the polarizer (P) and analyzer (A) directions.

The phase behaviours of 1 to 5 w/v% 5CB/SiO_2 on different applied temperature were investigated. The bright images of liquid crystal can be seen during nematic phases and become clearer as the concentration of SiO_2 gradually increased. The texture of nematic phase revealed the presence of birefringence due to its optical anisotropic nature by polarized microscope at 25.0 °C. Increase concentrations of SiO_2 led to the formation of aggregate-liked compounds that distributed in the liquid crystal host. The dark background indicated the existence of the liquid crystal domains in which this can be seen **in Figure 4 at** 25.0 °C. When light was polarized to liquid crystal in different index of refraction, colour was changed. The phase transition between nematic to isotropic were happen at temperature range from 3.45 to 3.47 °C as shown in Figure 4. We observed that the addition of SiO_2 up to 5 w/v% into liquid crystal host was significantly decreases the temperature of the nematic-isotropic transition to 2.0 °C. Therefore, high concentration of the SiO_2 will able to enhance the optical properties of liquid crystals by making the transition phase occurred in lower temperature range. Further increase in temperature produced dark regions that covered most entire area and reduced the birefringence. The image of isotropic is shown at temperature around 35.0 °C. The isotropic phase was described as the light passing through the molecules have not undergo rotation of its polarization plane due to the line-up of the molecules towards the field.

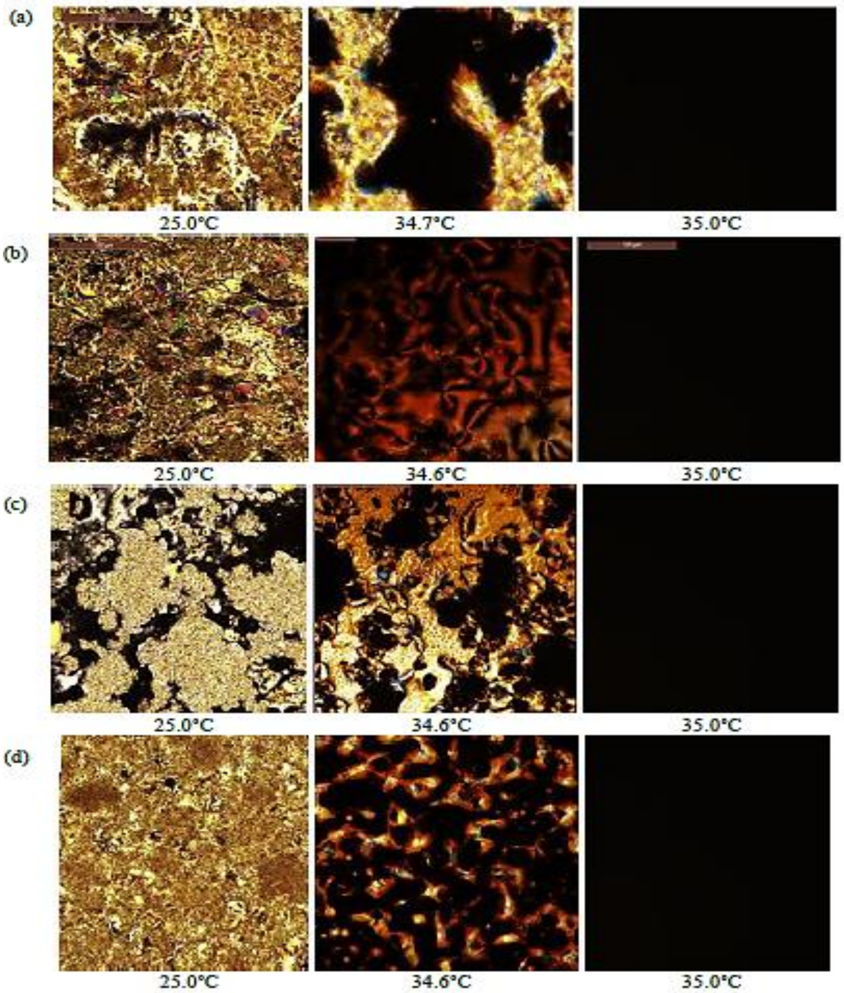


Figure 4. Phase behaviors of liquid crystal affected by different concentrations of SiO_2 at certain temperature range during heating process: (a) 1 w/v% of SiO_2/5CB (b) 2 w/v% of SiO_2/5CB (c) 3 w/v% of SiO_2/5CB (d) 4 w/v% of SiO_2/5CB and (f) 5 w/v% of SiO_2/5CB

Figure 5 shows the transition phase of hybrid 5CB/SiO2 sample during cooling process. As shown in Figure 5, the phase transition from isotropic to nematic phase occurred at certain temperature. Nematic phase appeared when the sample was let to cool, and this was determined by formation of colored bubbles [9]. During this phase transition, the small nematic droplets or known as bubbles begin to grow from the liquid until all the materials were nematic. The examples were given in the picture of Figure 5. Different colors were observed due to the birefringence of the nematic phase. In the Figure 5 (c), the schlieren texture of four brushers can be seen in the picture that represents the existent of nematic phase.

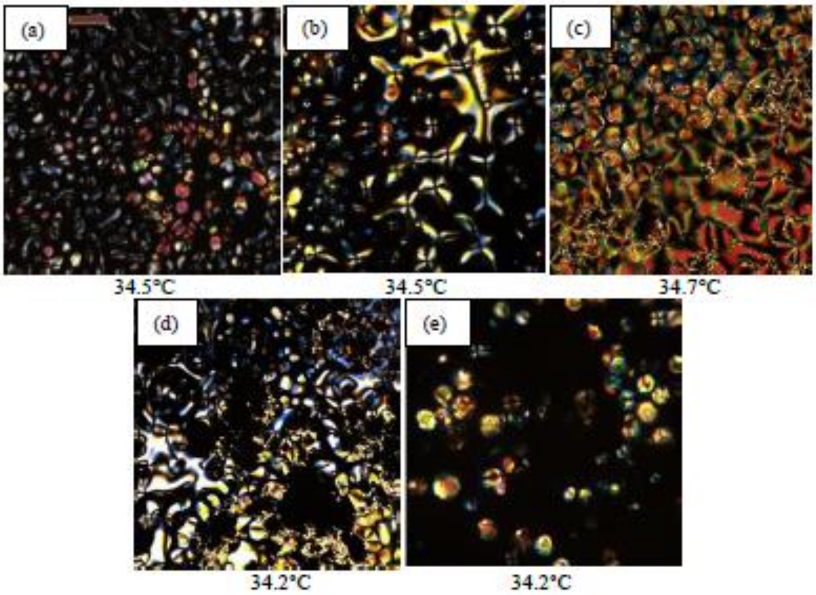


Figure 5. Images captured by POM during phase transition from isotropic to nematic phase at certain range of temperature during cooling process: (a) 1 w/v% of SiO_2/5CB (b) 2 w/v% of SiO_2/5CB (c) 3 w/v% of SiO_2/5CB (d) 4 w/v% of SiO_2/5CB and (f) 5 w/v% of SiO_2/5CB.

3.3. Characterization of Liquid Crystal by Electron Spin Resonance (ESR)

The director alignment of liquid crystal is vital in electro-optical display applications. In this study, the director distribution of liquid crystal was studied in the dispersions containing particle of silica using ESR. The effect of silica addition in liquid crystal host was determined.

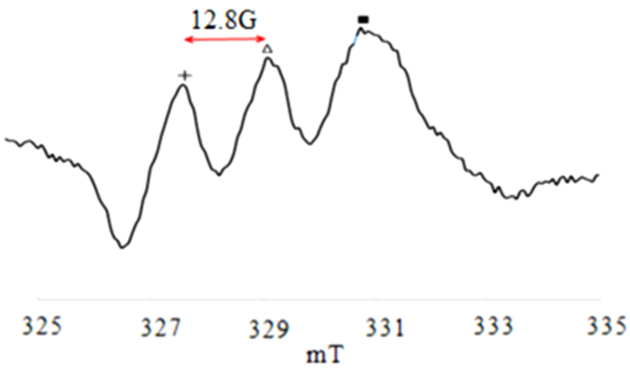


Figure 6. ESR spectrum of TEMPO in 5CB. The symbol +, Δ and ▪ are the hyperfine tensor at lower magnetic field, centre magnetic field and higher magnetic field

The ESR spectrum of pure 5CB was obtained by introduced with 2,2,6,6-tetramethyl-1-piperidinyloxyl (TEMPO) as a spin probe in which this spin probe was let to diffuse in the suspension. As mention before, 5CB liquid crystal was diamagnetic that cannot be detected by ESR. Thus, the ESR spectrum was generate based on the TEMPO direction and behavior where it mimics the crystal arrangement of its surrounding. The peak showed the line shape of 5CB as in **Figure 6** have a hyperfine spacing of 1.28 mT (12 G). This indicated that the liquid crystal director orientation was aligned in between of parallel and perpendicular to the magnetic field. However, this kind of spectrum was observed as powder pattern since the intensity and the amplitude were not really sharp and the small amount of spin probe introduced could affected towards the intensity of the peak.

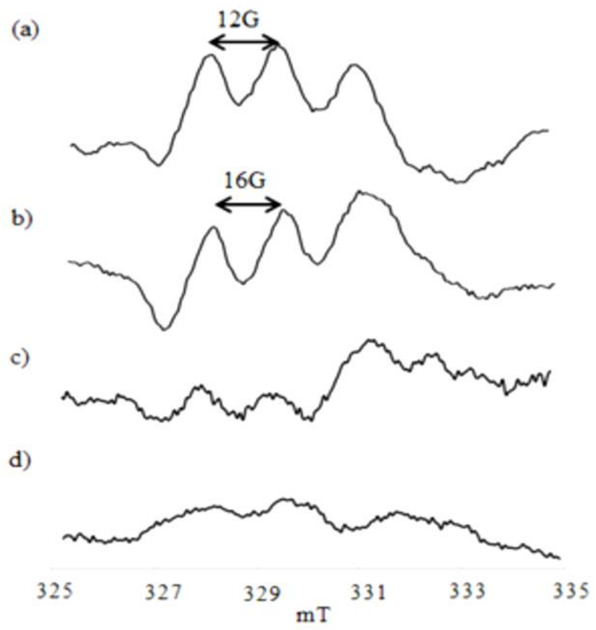


Figure 7. ESR signals of TEMPO for (a) pure 5CB; (b) low concentration of 1% w/v of SiO_2/5CB (c) medium concentration of 3%w/v of SiO_2/5CB (d) high concentration of 5 w/v% of SiO_2/5CB

ESR spectra of TEMPO spin probe in pure liquid crystal (5CB) and three different concentrations of SiO_2/5CB are shown in **Figure 7**. The angle of the liquid crystal aligned in the suspension will affect the hyperfine lines by applying the magnetic field. It shows the ESR line shape changes significantly with the increasing of the silica concentration. Even at low concentration of silica, the ESR spectrum showed significantly changes in the line shape, at which the hyperfine spacing was resulting with 1.6mT (16G). This indicated the liquid crystal director at low concentration, 1% w/v of SiO_2 was aligned in between of parallel and perpendicular to the magnetic field. Additionally, based on the intensities of hyperfine tensors (+, Δ and ▪) of 1 w/v% of SiO_2/5CB, the decrease of liquid crystal director that aligned parallel to magnetic field was observed when the SiO_2 was added to the LC host.

By introduced small amount of TEMPO in the sample, the amplitude and integral intensities of the spectrum will appear less sharp. Therefore, powder pattern of ESR spectrum can be observed. The powder pattern line shape was observed at medium concentration of 3 w/v% SiO2/5CB and high concentration of 5 w/v% SiO2/5CB. Further addition of SiO_2 into the liquid crystal host up to 5 w/v% caused the broaden of line shape in the ESR spectrum as shown in Figure 7 (c) and (d). The intensity of hyperfine tensors became extremely broad hence, the hyperfine spacing was not able to be determined. In high concentration of SiO_2, it is hard for spin probe to diffuse in the concentrated suspension where it might contain various of crystal orientation and alignment in one system. Larger time taken are needed for ESR to generate the spectrum and the timescale is exceeding the average scanning time of ESR. Hence, make the spectrum hard to analyze.

4. CONCLUSION

Silica colloidal liquid crystal was formed in this study by using silica as dispersed particles that suspended throughout the liquid crystal, 4-cyano-4‟-pentylbiphenyl (5CB) during isotropic phase. The colloidal liquid crystal was successfully produced with various sets of silica of different concentrations from 1 to 5 w/v%. The phase behavior of these silica colloidal liquid crystals was characterized by three different techniques, which are ATR-IR, POM and ESR. Based on IR spectra for all samples including pure 5CB and the hybrid systems revealed the presence of same functional groups in the compounds were caused by physical interaction and not involving chemical interaction. Besides, the phase transition of liquid crystal and the hybrid system were determined at certain temperatures range and the presences of birefringence were studied using POM. The phase variance shows the presence of isotropic-nematic liquid crystalline phase with the existence of schlieren textures in which nematic phase rise at temperature 25.0 °C. Clearer image of two and four brushes of schlieren textures can be seen at temperature below 35.0 °C. Finally, ESR technique was able to determine the director alignment of liquid crystal affected by the silica concentration. By increasing the concentration of silica up to 5 w/v%, powder pattern was finally observed. The director alignment of pure 5CB and the suspension of 1 w/v% of SiO2/5CB were aligned in between of parallel and perpendicular to the magnetic field with hyperfine spacing of 12 G and 16 G.

REFERENCES

[1] Nozawa, T., Brumby, P. & Yasuoka, K., Int. J. Mol. Sci. 19, 2715-2910 (2018).
[2] Kim K. H., & Song, J. K., NPG Asia Mater. 1, 29-41 (2009).
[3] Kawasumi, M., Hasegawa, N., Usuki, A. & Okada, A., Mater. Sci. Eng. C. 6, 135-143 (1998).
[4] Stannarius, R., Nature mater. 8, 617-681 (2009).
[5] Duijneveldt, J. S. V., Klein, S., Leach, E. & Pizzey, C., J. Phys- Condens Mat. 17, 2255-3122 (2015).
[6] Wang, X. & Zhou, Q., Liquid Crystalline Polymers. World Scientific Publishing Company. 6, 829-834 (2004).
[7] Nehring, J. & Saupe, A., J. Chem. Socie. Mol. Chem. Phys. 68, 1-15. (1972).
[8] Chen, W. T., Chen, P. S. & Chao C. Y., Japan. J. App. Phys. 48, (2009).
[9] Kowalewski, J. & Maler, L., CRC press, 457-682 (2017).